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Determination of chlorine, bromine, and sulfur in polyethylene materials using combustion ion chromatography

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Keywords
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Goal

To develop a combustion ion chromatography (CIC) method for the determination of chlorine, bromine, and sulfur in all forms of plastic materials

Introduction

Polyethylene (PE) is a thermoplastic created from the polymerization of ethylene, a process that produces long, straight chains of hydrocarbon monomers. By adjusting the polymerization process, different kinds of polyethylene with varying degrees of branching in their molecular structures can be made. The most common are linear, low-density polyethylene (LLDPE), low density polyethylene (LDPE), high density polyethylene (HDPE), and ultrahigh molecular weight polyethylene (UHMWPE). Polyethylene is widely used in packaging (plastic bags, plastic films, containers including bottles, etc.). Plastic materials do not consist only of plastic polymers. A large number of additives may be used to improve different properties of

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the plastic.[1] Some additives prevent degradation of the polymer during processing (typical for polyvinyl chloride (PVC)), while others improve resistance to fire or prevent degradation by environmental factors (e.g., UV, temperature, humidity, microorganisms). Halogen- and sulfur-containing compounds are often added as plasticizers, flame retardants, and heat stabilizers. Due to the widespread use of plastic/polymers and their subsequent impact on the environment, it is important to know the content of the halogens and sulfur when polyethylene materials are disposed of or recycled. Many countries throughout the world are adapting to regulate these substances.[2]

Plastic samples can be very difficult to analyze as sample preparation is required to extract analytes or remove interfering matrices, and these sample preparation techniques can be labor intensive. Combustion ion chromatography (CIC) has been demonstrated for determination of halogens and sulfur in a variety of difficult samples, including coal.[3] In this application note, we demonstrate that a CIC system can be used for automated qualitative and quantitative analysis of halogens and sulfur in plastic samples. Four plastic samples were analyzed for their chlorine (Cl), bromine (Br), and sulfur (S) contents. Method accuracy was evaluated using a polymer certified reference material (ERM EC680k) for Cl, Br, and S and spike recovery experiments for each analyte.

Experimental

Equipment

- Thermo Scientific™ Dionex™ Integrion™ HPIC™ system including the following:
  - Dionex Integrion HPIC System Pump
  - Eluent Generation
  - Column Oven Temperature Control
  - CD Conductivity Detector
  - Detector Compartment Temperature Control
- Thermo Scientific™ Dionex™ AS-AP Autosampler with 10 mL vial trays
- Mitsubishi Automatic Combustion Unit Model AQF-2100H system, comprised of the following:
  - Electric Furnace HF-210
  - Gas Absorption Unit GA-210
  - External Solution Selector ES-210
  - Automatic Boat Controller ABC-210

Consumables

Table 1 lists the consumable products needed for the Dionex Integrion HPIC system, configured for suppressed conductivity detection.

Instrument setup and installation

Follow TN72211 to set up the system.[4] For this application, the sample loop is installed on the Dionex Integrion HPIC system injection valve instead of using the injection valve in the Mitsubishi GA-210 module (Figure 1). This setup allows the use of high pressure ion chromatography and reduces the gradient delay.

The Dionex Integrion HPIC system is a high-pressure-capable integrated reagent-free ion chromatography (RFIC™) system designed for high-pressure eluent generation under conditions up to 5000 psi. The details on preparing an IC system for the analysis can be found in TN175.[5] The key steps include:

- Configuring the modules in the Thermo Scientific™ Chromeleon™ chromatography data system (CDS) software
- Plumbing the high pressure Dionex Integrion HPIC system
- Conditioning electrolytic devices and columns according to their product manuals
- Starting the Dionex Integrion HPIC system
- Creating an Instrument Method

Table 1. Consumables list for the Dionex Integrion HPIC system.

Product Name	Product Description	Part Number
Thermo Scientific™ Dionex™ IC PEEK Viper™ Fitting Tubing Assembly Kits	Dionex IC Viper fitting assembly kit for the Integrion: Includes one each of P/Ns: 088805–088811	88798
Dionex IC PEEK Viper Fitting Tubing Assemblies	Guard to separator column: 0.007 in i.d., 4.0 in long (102 mm)	88805
	Injection Valve, Port C (Port 2) to guard column: 0.007 in i.d., 5.5 in long (140 mm)	88806
	EGC Eluent Out to CR-TC Eluent In: 0.007 in i.d., 6.5 in long (165 mm)	88807
	Separator column to Suppressor Eluent In: 0.007 in i.d., 7.0 in (178 mm)	88808
	Suppressor Eluent Out to CD In: 0.007 in i.d., 9.0 in long (229 mm)	88810
	CR-TC Eluent Out to Degasser Eluent In: 0.007 in i.d., 9.5 in long (241 mm)	88811
Dionex AS-AP Autosampler Vials	Package of 100, polystyrene vials, caps, blue septa,10 mL	74228
Thermo Scientific™ Dionex™ EGC 500 KOH Potassium Hydroxide Eluent Generator Cartridge	Eluent generator cartridge	75778
Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column	Continuously regenerated trap column used with Dionex EGC 500 KOH cartridge	88662
HP EG Degasser Module	Degasser installed after Dionex CR-TC trap column and before the injection valve. Used with eluent generation.	75522
Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor	Suppressor for 2 mm columns, using recycle mode	82541
Thermo Scientific™ Dionex™ IonPac™ AG11-HC-4µm Guard Column	Anion guard column, 2 × 50 mm	78036
Dionex IonPac AS11-HC-4µm Analytical Column	Anion analytical column, 2 × 250 mm	78035
Thermo Scientific™ Nalgene™ Syringe Filter	Syringe filters, 25 mm, PES membrane, 0.2 µm. This type is compatible with IC analysis.	Thermo Scientific 725-2520*

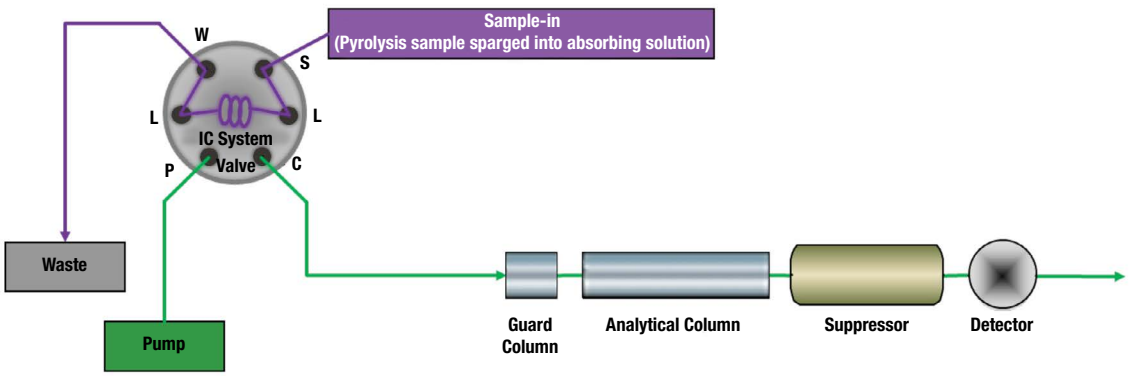

Figure 1. Direct injection using the Dionex Integrion IC System injection valve.

Reagents and Standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ•cm resistance or better
- Thermo Scientific™ Dionex™ Combined Seven Anion Standard I, 50 mL (P/N 056933)
- Thermo Scientific™ Dionex™ Chloride Standard (1000 mg/L), 100 mL (P/N 037159)
- Thermo Scientific™ Dionex™ Sulfate Standard (1000 mg/L), 100 mL (P/N 037160)
- Potassium bromide, Crystal BAKER ANALYZED® ACS Reagent (P/N 2998-01)
- European Reference Material ERM®- EC680k Polyethylene (Trace Elements Low Level), ~100 g, ARMI/LGC Standards

Table 2A. Combustion parameters.

AQF-2100H	
Sample size	~20–35 mg (2–3 pellets)
Sample boat	Quartz
Pyrolysis tube	Quartz tube / Quartz wool
Absorption solution	H_2O_2 aqueous solution (mg/L)
Mode	Constant volume
HF210	
Furnace inlet temperature	900 °C
Furnace outlet temperature	1000 °C
Argon flow (Carrier)	200 mL/min
Oxygen flow (Combustion agent)	400 mL/min
GA-210	
Absorption tube	10 mL
Final absorption solution volume	10 mL
Absorption solution volume*	3.5 mL
Water supply scale	3
Argon flow for humidification	100 mL/min
Washing parameters	
Water injection time	20 s
Drain time	12 s
Washing times	3
Gas line washing time	0.5 s
Gas line washing interval	3 s
Gas line washing times	3
Washing time of sample absorption line	5 s
Syringe washing times	3
Gas line collection parameter	
Collection time	0.5 s
Collection interval	3.0 s
Times	3
Injection parameters	
Washing time for injection start	0 s
Sample purge time	5 s
Sample absorption time	10 s

*This is the starting absorption volume. Final absorption volume is adjusted to a constant about 10 mL and is determined accurately according to the manual[5].

Table 2B. ABC210/ ASC-250L parameters.*

Position (mm)	Wait time (s)	Speed (mm/s)
130	90	20
160	90	0.12
End	90	20
Cool	60	40
Home	120	40

*Argon time 10 s, Oxygen time 600 s.

Table 3. Ion chromatography parameters.

System	Dionex Integrion HPIC System
Columns	Dionex IonPac AS11-HC-4µm, Analytical, 2 × 250 mm Dionex IonPac AG11-HC-4µm, Guard, 2 × 50 mm
Eluent	25 mM KOH
Eluent Source	Dionex EGC 500 KOH cartridge with high pressure CR-ATC
Flow Rate	0.38 mL/min
Sample Loop	100 µL
Column Temp.	30 °C
Compartment Temp.	15 °C
Detection	Suppressed conductivity with Dionex ERS 500 Electrolytically Regenerated Suppressor, recycle mode
Suppresser Current	24 mA
System Backpressure	~4050 psi
Background Conductance	~0.1–0.2 µS/cm
Noise	0.2–0.4 nS/cm peak-to-peak
Run Time	10 min

Preparation of solutions and reagents

1000 mg/L stock chloride solution

Use Dionex Chloride Standard (1000 mg/L), 100 mL (P/N 037159) or prepare your own standard.

1000 mg/L stock sulfate solution

Use Dionex Sulfate Standard (1000 mg/L), 100 mL (P/N 037160), or prepare your own.

1000 mg/L stock bromide solution

Weigh 0.149 g of dry potassium bromide in a 125 mL polypropylene bottle and tare the balance. Add 100 g of DI water to make a 1000 mg/L bromide stock solution. Cap the bottle and shake to completely dissolve the solid material. The standard is stable for one week when stored at 4 ˚C.

Working Standard Solutions

Deliver the appropriate volume of the 1000 mg/L stock solution into a 125 mL polypropylene bottle and bring to volume (by weight) with DI water. For this application, calibration standards were prepared at 0.1, 0.2, 0.4, 0.5, 0.75, and 1.25 mg/L. Aliquots were stored at –40 ˚C and thawed prior to use.

Results and discussion

By using a combustion ion chromatography (CIC) system consisting of an automatic quick furnace AQF-2100H and a Dionex Integrion HPIC system, the concentrations of halogens and sulfur were determined in plastic materials. Combustion and IC parameters used for this application are listed in Tables 2 and 3. About 20–35 mg of plastic sample was weighed in a quartz sample boat and introduced into the system, where it was thermally decomposed in an argon (Ar) atmosphere, then combusted in an oxygen atmosphere. Halogens in the sample were converted to hydrogen halide and halogen gas and sulfur was converted to sulfur oxide. These components were collected into absorbing solution and converted to halide ion and sulfate ion. For sulfur-containing samples, hydrogen peroxide was added in the absorbing solution to oxidize hydrogen sulfite, resulting from the incomplete oxidation of sulfur, which was quantified as sulfate in aqueous solution. The resulting solution was analyzed by injecting into an IC system. Figure 2 shows the chromatogram of the combusted plastic certified reference material (ERM-EC680k) containing the anions fluoride, nitrite, sulfate, bromide, and nitrate separated using a Dionex IonPac AS11-HC-4µm column. The run time was 10 min using an isocratic condition. The concentrations of anions were calculated using calibration method 1, discussed below in the Calibration section.

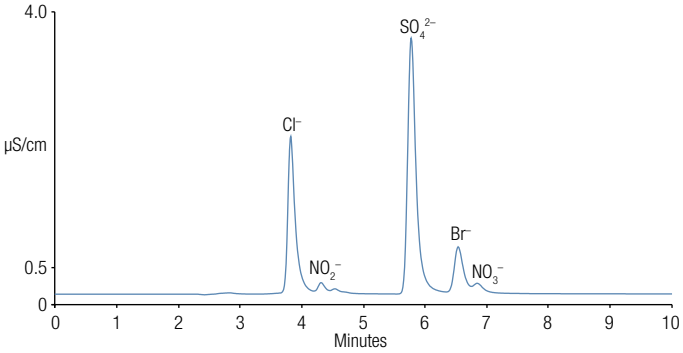

Figure 2. Chromatogram of ERM EC680k.

Calibration

There are two methods for calibration. Method 1 uses direct injection of liquid standards through the External Solution Selector ES-210. In this method, calibration standards containing the components of interest are injected and measured directly through IC. Using the calibration curve of each component, the concentration of component in the sample is calculated using the formula below:

$$Concentration\ (mg/L) = Cc * A * \frac{1}{S} * 1000$$

Cc is Component concentration (mg/L), A is Absorption solution at constant volume (mL), and S is Sample weight in mg. Absorption solution at constant volume is determined following instructions in the Mitsubishi Automatic Combustion Unit Model AQF-2100H manual.[6] The dilution factor is approximately 10,000 when a 10 mL absorption tube is used. The weight of sample (S) and dilution factor (A*1000) are then entered into the data sequence pane of the Chromeleon CDS software console window which automatically calculate the concentration of component in the sample.

Method 2 uses injection of liquid standards through the Liquid Sample Changer Module ASC-250L. In this method, standard solution prepared with organic solvent is injected into the combustion unit where it is first combusted and then measured by ion chromatography. Using the calibration curve of each component, the concentration of component in the sample is calculated:

$$Concentration\ (mg/L) = Cc * \frac{1}{S}$$

Because both the standards and samples are combusted in the same way, the dilution correction factor is not needed. Only the weight of each sample is entered into the data sequence pane of the Chromeleon CDS software.

Sample analysis

Four plastic materials, listed in Table 4, were analyzed for their Cl, Br, and S contents. Figure 3 shows chromatograms of four plastic samples. Besides chloride and sulfate, fluoride, nitrite, and nitrate are also observed in these samples. Bromide was not found in any of the four samples analyzed. This may be because bromide is no longer used as an additive in plastics as a result of its toxicity. Sample 2 (transfer pipette) was found to contain very little chloride and sulfate. In all four samples, sulfate was found to be in low concentration with the exception of Sample 3 (plastic wrap) where it is almost ~55 mg/L. Plastic wrap contains mostly PVC material, and PVC has high amounts of sulfur-containing organotin compounds used as heat stabilizers.

Table 4. List of plastic materials used in this study.

Sample Number	Sample	Polymer Type
1	Wash bottle	LDPE
2	Transfer pipette	LDPE
3	Plastic wrap	Mostly PVC
4	Bubble wrap	LDPE or HDPE

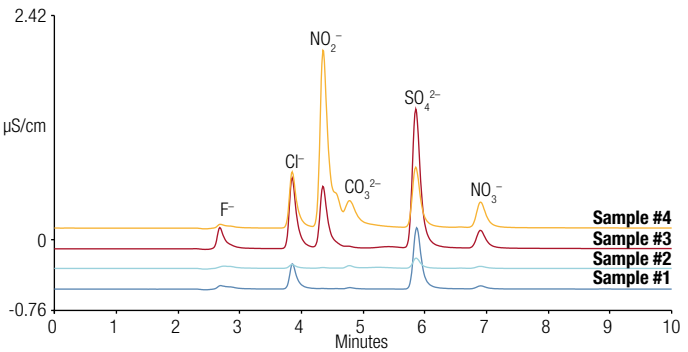

Figure 3. Chromatogram of four polymer samples.

Precision and accuracy

The precision and accuracy for Cl, Br, and S were evaluated using a certified reference material of low-density polyethylene (EC680k), by European Reference Materials (ERM, Belgium) purchased from ARMI/LGC Standards. Table 5 lists the amount of Cl, Br, and S along with their certified values. The percent relative standard deviation (RSD) is less than 2.4% for all three anions indicating good precision. The recovery is 95–105%.

Table 5. Amount of chlorine, bromine, and sulfur in ERM EC680k.

	Chlorine (mg/L)	Bromine (mg/L)	Sulfur (mg/L)
1	98.1	96.9	78.3
2	98.0	91.7	77.0
3	98.2	95.6	78.4
4	97.5	94.8	81.2
5	96.7	93.6	78.5
6	94.8	96.6	77.3
7	97.8	98.4	78.9
Average	97.3	95.4	78.5
RSD	1.25	2.36	1.74
Certified value	102	96	76
% Recovery	95.4	99.3	103

Recovery

For the recovery experiment, the plastic sample was spiked with CRM pellets and the percentage recovery was calculated using the equations below:

$$Recovery\ \% = \frac{C\ spiked\ sample - C\ unspiked\ sample}{C\ added} * 100$$

$$C\ spiked\ sample = Cc * A * \frac{1}{Weight\ of\ plastic\ sample} * 1000$$

$$C\ unspiked\ sample = Cc * A * \frac{1}{Weight\ of\ plastic\ sample} * 1000$$

$$C\ added = Cc * A * \frac{1}{Weight\ of\ CRM\ pellet} * 1000$$

where *Cc* is component concentration (mg/L) obtained from the chromatogram, *A* is absorption solution at constant volume (mL) determined following instructions in the Mitsubishi Automatic Combustion Unit Model AQF-2100H manual.[5]

Figures 4, 5, 6, and 7 are the chromatograms of the spiking experiment for samples 1, 2, 3, and 4, respectively. Table 6 contains spike recovery results for chloride and sulfate in four plastic samples. The percent recovered ranged from a low of 91.7% to a high of 107% for chloride and 80.8% to 115% for sulfate.

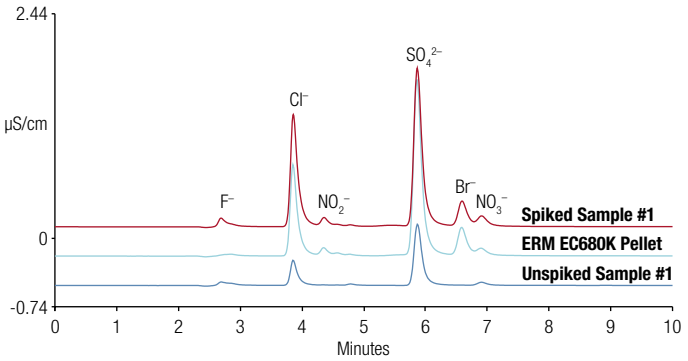

Figure 4. Chromatogram of unspiked sample 1, ERM EC680k pellet, and sample 1 spiked with ERM pellet.

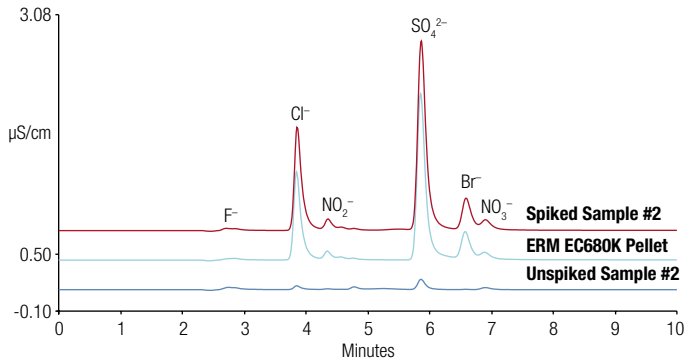

Figure 5. Chromatogram of unspiked sample 2, ERM EC680k pellet, and sample 2 spiked with ERM pellet.

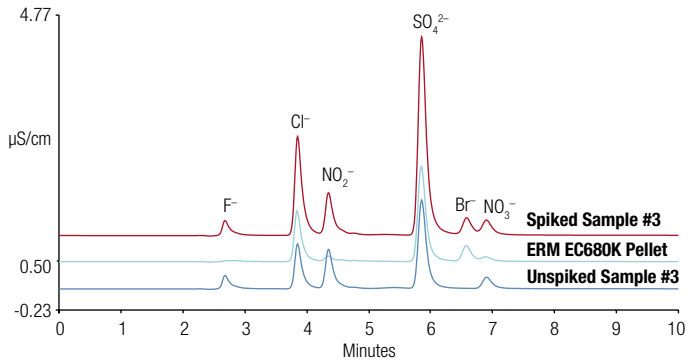

Figure 6. Chromatogram of unspiked sample 3, ERM EC680k pellet, and sample 3 spiked with ERM pellet.

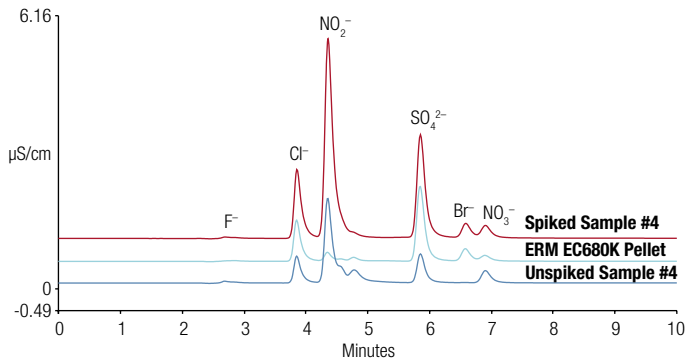

Figure 7. Chromatogram of unspiked sample 4, ERM EC680k pellet, and sample 4 spiked with ERM pellet.

Table 6. Spike recovery for samples 1, 2, 3, and 4.

	Unspiked (mg/L)	Added (mg/L)	Spiked (mg/L)	Recovery (%)
Sample 1				
Chlorine	23.7	97.5	128	107
Sulfur	19.8	83.2	87.1	80.8
Sample 2				
Chlorine	12.2	96.7	102	92.5
Sulfur	3.5	78.5	87.0	106
Sample 3				
Chlorine	61.4	94.8	148	91.7
Sulfur	54.9	77.3	144	115
Sample 4				
Chlorine	43.5	97.8	142	101
Sulfur	20.1	78.9	102	104

Conclusion

The results demonstrate that the CIC system can be used for both qualitative and quantitative analysis of Cl, Br, and S in plastic samples. The method was further validated using certified reference material ERM EC680k with recoveries from 95% to 105%. This automated method is highly sensitive, easy to use, saves time, and produces fewer environmental contaminants than other sample preparation procedures, such as acid digestions or back extractions from organic solvents. This analysis will allow polymer manufacturers to monitor halogen/sulfur concentration levels to ensure compliance with government regulations. The HPIC system allows for faster IC analysis, thereby shortening the overall CIC method. The same system, the Dionex Integrion HPIC, also makes its own potassium hydroxide eluent and regenerant for suppressed conductivity detection, thereby eliminating errors and ensuring high chromatographic reproducibility.

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Find out more at **thermofisher.com/combustionIC**

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